

9 Getting Started in Synthesis: A Tabular Guide to Selected Monofunctional Fluorous Compounds

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9.1 Introduction

The first steps when beginning a fluorous project are to purchase the necessary fluorous starting materials and synthesize the target molecules. The vendors of fluorous solvents listed in Table 3-1 also provide a number of fluorous building blocks, as does Fluorous Technologies Inc. (FTI, <http://fluorous.com/index2.html>). This chapter, augmented by the references to the table of partition coefficients in Chapter 6 (Table 6-1), is intended as a guide to the synthesis of simple fluorous molecules. It is by no means comprehensive, but does provide many useful leads for researchers just beginning in this field.

Looking first backwards to Table 6-1, it is easy to visually scan various families of functional groups and locate lead references. However, if the partition coefficient has not been measured, the molecule is not included. Furthermore, superior syntheses may have been developed after the initial literature report.

Recognizing this gap, this chapter summarizes a wide range of monofunctional “heavy” fluorous compounds and selected “light” fluorous compounds in a tabular form. In most cases, abbreviated synthetic details are indicated (“ \Rightarrow ” symbol), followed by the literature reference. In some cases, particularly useful reactions are indicated (“ $\bullet +$ ” symbol). More complex target molecules can then be assembled from perfluoroalkyl- and organic groups of appropriate topologies, sometimes inserting “insulator” groups between these constituents (cf. Chapters 4 and 5).

The latter strategy or modular synthesis calls for an “*F*-tool-kit” suitable for the most diverse applications. At one extreme, various target *F*-entities with linear perfluoroalkyl groups exhibit good organic solubilities under reaction conditions at higher temperatures, but quantitatively precipitate at lower temperatures (thermomorphism). At the other extreme *F*-derivatives with flexible and branched perfluoropolyether type substituents could have rather wide fluid temperature ranges (high-tech lubricants).

Syntheses involving highly fluorinated compounds will certainly provide simultaneous feelings of frustration and pleasure for those so engaged. This derives from differences in reactivity and solubility patterns from those experienced in traditional organic chemistry. The high electronegativity of fluorine atoms and perfluoroalkyl-groups strongly affect reac-

Handbook of Fluorous Chemistry. Edited by John A. Gladysz, Dennis P. Curran, István T. Horvath
Copyright © 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 3-527-30617-X

tion centers, unless appropriately positioned (cf. Chapter 5). Moreover, macroscopic properties, such as solubility, fluorophilicity, volatility, melting and boiling point, transition enthalpies, etc. are all governed by the composition and structure of the molecules. The higher their fluorine character, the more unique properties will be expressed.

The trifluoromethyl group, which can be regarded as the shortest *F*-ponytail, appears in the Beilstein database with a frequency one order of magnitude greater than all longer R_{fn} segments combined ($R_{f1}GH^*/R_{f2-24}GH^* = 205\,000:24\,000$). Hence, some prototype chemistries known only for CF_3 -compounds are also displayed in the Tables. In the first series of Tables, molecules without hydrogen atoms are collected. In the second, hydrogen atoms of all descriptions are allowed.

Series I [no hydrogen included]

9.1.1 Perfluoroalkanes, perfluoroalkenes and perfluoroalkynes

9.1.2 Perfluoroalkyl halides and related compounds

9.1.3 Perfluoroethers, perfluoroalkanones and perfluoroalkanecarboxylic acid halides

9.1.4 Perfluoroalkylsulfides and disulfides, perfluoroalkanesulfonyl halides and anhydrides

9.1.5 Tris(perfluoroalkyl)amines, perfluoroazomethines, perfluoroalkanecarbonitriles, tris(perfluoroalkyl)triazines and perfluoroalkyl isocyanates

9.1.6 Perfluoroalkylmagnesium-, zinc-, copper(I)-, lithium-, and caesium intermediates.

Tab. 9.1-1. Perfluoroalkanes, perfluoroalkenes and perfluoroalkynes

Compound [C,F]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
C_nF_{2n+2} , <i>cyclo</i> - C_nF_{2n} , etc.	⇒ •+ Disclosure of a "Secret World": Properties of Fluorocarbons	1
Perfluoroalkanes	⇒ •+ Synthesis and Chemistry of Perfluoroalkanes. A Review	2
$CF_3CF_2CF=CF_2$	•+ $KF + ROCH_2Cl/PTC, rt. \rightarrow ROCH_2C(CF_3)_2CF_2CF_2CF_3$ (82%)	3
$CF_3(CF_2)_3CF=CF_2$	⇒ $R_{f6}CO_2Na$ /heating $\rightarrow R_{f4}CF=CF_2$ + isomers, in a 73:27 ratio	4
$R_{fn}CF=CF_2$, $n = 1, 2, 3, 5, 7$	⇒ Prepared by the pyrolysis of the salts of $R_{fn+2}CO_2H$'s	5
$(CF_3)_2C=CF_2$	⇒ <i>cyclo</i> - $C_4F_8/25\,s$ at $710\text{--}730\,^\circ C$ \rightarrow yield: 45%, bp = $6\text{--}9\,^\circ C$	6
$R_{fn}C=CR_{fm}$, $n = 2, 4, 8$; $m = 4, 6, 8$	⇒ $R_{fn}C\equiv CH + R_{fm}I/220\,^\circ C \rightarrow R_{fn}CI=CHR_{fm}/base-PTC \rightarrow$	7

Tab. 9.1-2. Perfluoroalkyl halides and related compounds

Compound [C,F,X]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
R _{fn} I, n = 1, 3	⇒ R _{fn} CO ₂ Na + I ₂ /DMF, reflux → yield: 70–80%	8
R _{fn} I, n = 1–12	⇒ Ref. 9. Uses and reactions of: Ref. 10	9, 10
(CF ₃) ₂ CF(CF ₂ CF ₂) _n I	⇒ (CF ₃) ₂ CFI + CF ₂ =CF ₂ /175 °C → mix of telomers; n = 1 > n = 2–4	11
Cl(CF ₂) _n I, n = 2, 4, 6	• + CH ₂ =CHR/acid treated Fe catalyst → Cl(CF ₂) _n CH ₂ CH(I)R	12
C ₈ F ₁₇ Br	⇒ C ₈ F ₁₇ H + CBr ₄ /300 °C, 24 h → yield: 40%	13
C ₈ F ₁₇ Cl	⇒ C ₈ F ₁₇ H + CCl ₄ /350 °C, 24 h → yield: 31%	13
X(CF ₂) _n Cl	• + CH ₂ =CHR/(NH ₄) ₂ S ₂ O ₈ -HCO ₂ Na → X(CF ₂) _n (CH ₂) ₂ R (70–80%)	14
R _{f6} CCl ₃	⇒ R _{f6} I + CCl ₄ /Zn, EtCO ₂ H, CH ₂ Cl ₂ , 2 h → yield: 51%	15
R _{f9} CCl ₃	⇒ R _{f10} I + AlCl ₃ /~115 °C, 28 h → yield: 55%	16
(CF ₃) ₂ CFO(CF ₂) ₃ CCl ₃	⇒ (CF ₃) ₂ CFO(CF ₂) ₄ I + AlCl ₃ /100 °C, 63 h → yield: 43%	16
CCl ₃ (CF ₂) ₄ N=N(CF ₂) ₄ CCl ₃	• + SO ₃ /H ₂ SO ₄ /Hg ²⁺ → HO ₂ C(CF ₂) ₄ N=N(CF ₂) ₄ CO ₂ H, yield: 95%	17
(CF ₃ CF ₂) ₂ NCF ₂ CF ₂ I	⇒ (CF ₃ CF ₂) ₂ NCF ₂ CF ₂ COF/LiI, 180 °C, 18 h → yield: 72%	18
CF ₃ (CF ₂) ₇ OCF ₂ CF ₂ I	⇒ R _{f7} COF + CF ₂ =CF ₂ /KF, diglyme, –196 °C, 7 d →	19
C ₃ F ₇ OCF(CF ₃)CF ₂ OCFICF ₃	• + PhI/Cu, bipy, DMSO → C ₃ F ₇ OCF(CF ₃)CF ₂ OCFPhCF ₃ (73%)	20
(CF ₃) ₂ CFOCF ₂ CF ₂ I	⇒ (CF ₃) ₂ CFOK + CF ₂ =CF ₂ + I ₂ or ICl/CH ₃ CN → bp = 86–87 °C	21
F ₅ SCF ₂ I	⇒ F ₅ SCF ₂ CO ₂ Ag + I ₂ /heating → yield: 54%	22
F ₅ SCF ₂ CF ₂ I	⇒ S ₂ F ₁₀ + ICF ₂ CF ₂ I + CF ₂ =CF ₂ /–196 to 155 °C/ → yield: 49%	23
F ₅ SCF ₂ CF ₂ Br	⇒ F ₅ SBr + CF ₂ =CF ₂ /90 °C, 2 d → bp = 60–62 °C	24
F ₅ SCF ₂ CF ₂ Cl	⇒ SF ₅ Cl + CF ₂ =CF ₂ /(PhCO) ₂ O ₂ , 90 °C, 10 h → yield: 22% to C ₂ F ₄	25
(CF ₃) ₃ GeI	⇒ Ref. 26. Commercially available	26

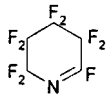
Tab. 9.1-3. Perfluoroethers, perfluoroalkanones and perfluoroalkanecarboxylic acid halides

Compound [C,F,O(X)]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
R _f CF(CF ₂) _n CF ₂ O, n = 2, 3	• + AlCl ₃ , heating → R _f CCl(CF ₂) _n CCl ₂ O	27
R _{f6} OR _{f6}	• + AlCl ₃ /185 °C, 14 h → R _{f5} COCl (63%) + R _{f5} CCl ₃ (51%)	28
R _f C(O)CF(CF ₃) ₂	⇒ R _f COF/CsF-catalyst + CF ₂ =CFCF ₃ → yield: 39–75%, R _f = (CF ₃) ₂ CF; C ₃ F ₇ , CF ₃ ; etc.	29
C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)COCF ₃	⇒ C ₃ F ₇ OCF(CF ₃)CF ₂ OCF(CF ₃)COF + CF ₃ SnMe ₃ / 140 °C, 20 h, sealed tube → yield: 49%	30
C ₇ F ₁₅ COCl	⇒ C ₇ F ₁₅ CO ₂ H + SOCl ₂ /DMF, heating, 4 h → yield: 90%	31
C ₃ F ₇ O[CF(CF ₃)CF ₂ O] _n CF(CF ₃)COF	⇒ CF ₃ CFCF ₂ O + KF/diglyme → acid fluorides, n = 1–4	32
C ₇ F ₁₅ COF	⇒ C ₇ F ₁₅ CO ₂ H + HCF ₂ CF ₂ N(CH ₃) ₂ /0–25 °C, 2 h → yield: 75%	33

Tab. 9.1-4. Perfluoroalkylsulfides and disulfides, perfluoroalkanesulfonyl halides and anhydrides

Compound [C,F,S(O,X)]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
(C ₃ F ₇) ₂ S	⇒ C ₃ F ₇ I + S _x /300 °C, 10 h → yield: 11%, bp = 88 °C	34
(C ₇ F ₁₅) ₂ S ₂	⇒ C ₇ F ₁₅ I + S _x /255 °C, 17 h → yield: 60%, mp = 39 °C, bp = 247 °C	34
C ₆ F ₁₃ SO ₂ Cl	• + C ₆ H ₆ /RuCl ₂ (PPh ₃) ₃ → C ₆ H ₅ C ₆ F ₁₃ , yield: 44%	35
C ₈ F ₁₇ SO ₂ X, X = F, Cl	⇒ Title compounds were obtained in ~98% purity from a mixture containing branched isomers by cooling to -20 °C and filtration of the crystalline linear isomers	36
R _{fn} SO ₂ Cl and/or (R _{fn} SO ₂) ₂ O	⇒ R _{fn} SO ₃ K + PCl ₅ ·2ZnCl ₂ → "high yield and purity". When PCl ₅ reacted with perfluoroalkanesulfonic acids, yields anhydrides	37
(cyclo-C ₂ F ₅ C ₆ F ₁₀ SO ₂) ₂ O	• Used for the thermal perfluoroalkylation of dyes (e.g., pyranthrone, Cu phthalocyanine) to yield fluorous derivatives for staining PTFE	38

Tab. 9.1-5. Tris(perfluoroalkyl)amines, perfluoroazomethines, perfluoroalkanecarbonitriles, tris(perfluoroalkyl)triazines and perfluoroalkyl isocyanates

Compound [C,F,N(O)]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
(C ₄ F ₉) ₃ N	• An inert medium for organic reactions	39
	⇒ Prepared by the defluorination of undecafluoropiperidine with steel wool at 500 °C/1 atm, yield: 40%	40
CF ₃ CF ₂ CF ₂ CF ₂ N=CFCF ₂ CF ₂ CF ₃	⇒ (C ₄ F ₉) ₃ N + SbF ₅ catalyst/120 °C, 4 h, (-C ₄ F ₁₀) → yield: 67%	41
C ₇ F ₁₅ CN	⇒ C ₇ F ₁₅ CONH ₂ + P ₂ O ₅ /200 °C → yield: 84%, bp = 103–104 °C	42
2,4,6-(C ₇ F ₁₅) ₃ -1,3,5-triazine	⇒ C ₇ F ₁₅ CN/aniline, 120–140 °C, 13 h → yield: 77%	43
R _{f3} NCO	⇒ R _{f3} N=NR _{f3} + CO/300 °C, 800 atm, 8 h → yield: 11% + C ₆ F ₁₄	44
R _{f7} NCO	⇒ R _{f7} COCl + Me ₃ SiN ₃ → yield: 82%	45

Tab. 9.1-6. Perfluoroalkylmagnesium- and perfluoroalkylzinc halides; perfluoroalkyl copper(I)-, perfluoroalkyl-lithium-, and perfluoroalkyl-caesium intermediates

Compound [C,F,Mg/Zn/Cu/Li/Cs]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$R_{f8}MgBr/THF$	⇒ $C_8F_{17}I + PhMgBr$ or C_2H_5MgBr/THF at $-70\text{ }^{\circ}C/ \rightarrow R_{f8}MgBr \rightarrow R_{f8}C(CH_3)_2OH$ or $R_{f8}C(CF_3)_2OH$, in 90 or 64% yields, resp.	46
$R_{fn}MgBr/ether, n = 4, 6, 8, 10$	⇒ $C_nF_{2n+1}I + C_2H_5MgBr/ether$ at $-35-40\text{ }^{\circ}C/ \rightarrow R_{fn}MgBr/ether$; quenched by $PhCH_2CH=O$ to yield $PhCH_2CH(OH)R_{fn}$.	47
$(CF_3)_2CF_2ZnI/THF$	• + $PhCOF/py \rightarrow PhCOCF(CF_3)_2$, yield: ~100%	48
$R_{fn}Cu.solvant$	⇒ $R_{fn}I + 2Cu/DMSO, 110-120\text{ }^{\circ}C, 2\text{ h} \rightarrow R_{fn}Cu$, yield > 80%	49
" $C_8F_{17}Li$ "/ether ($-78\text{ }^{\circ}C$)	⇒ Generated <i>in situ</i> : $C_8F_{17}I + CH_3Li-LiBr/ether, -78\text{ }^{\circ}C$	50
$CF_3CF_2CF_2C(CF_3)_2^-Cs^+$	• + $ArCH_2Br \rightarrow ArCH_2C(CF_3)_2R_{f3}$, 10 examples, yields: ~60%	51
Miscellaneous F-organometallics	⇒ • + Synthesis and reactivity of F-organometallics. A review	52

Series II [hydrogen included]

9.2.1 Hydroperfluoroalkanes, perfluoroalkylalkanes/cycloalkanes, perfluoroalkylalkenes and perfluoroalkylalkynes, perfluoroalkylarenes, (perfluoroalkyl)alkylarenes and related compounds

9.2.2 (Perfluoroalkyl)alkyl halides; perfluoroalkyl- and (perfluoroalkyl)alkyl aryl/benzyl halides

9.2.3 Perfluoroalkylalkanols and ethers

9.2.4 Fluorous mercaptanes, sulfides, sulfoxides, sulfonates, sulfonimides and selenides

9.2.5 Fluorous amines, anilines, pyridines; phosphines and phosphites

9.2.6 Fluorous boron-, silicon-, tin-, lithium-, zinc-, and magnesium compounds

9.2.7 Fluorous aldehydes and ketones

9.2.8 Fluorous carboxylic acids

9.2.9 Fluorous esters and carbonic acid derivatives

Acknowledgements

The author thanks the Hungarian Scientific Research Foundation (OTKA T 034871) and the European Contract of Research Training Network ('Fluorous Phase' HPRN-CT-2000-00002) for financial support.

Tab. 9.2-1. Hydroperfluoroalkanes, perfluoroalkylalkanes/cycloalkanes, perfluoroalkylalkenes and perfluoroalkylalkynes, perfluoroalkylarenes, (perfluoroalkyl)alkylarenes and related compounds

Compound [C,F,H]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
$R_{fn}CF_2H$ ($n = 2-4$)	⇒ $R_{fn}CF_2I + H_2$ /Raney Ni, 60 atm, 350 °C → yield: 80%	9a
$(CF_3)_3CH$	⇒ Prepared as described and its thermodynamic acidity studied	53
$F(CF_2)_8(CH_2)_8H$	⇒ $R_{f8}I + CH_2=CHC_6H_{13}$ /AIBN → $R_{f8}CH_2CH(I)C_6H_{13}$; + Zn/HCl in CH_3OH → title product, its gel formation from alcohols studied	54
CF_3 -cyclo- C_6H_{11}	⇒ • + As a new solvent? Limits of use	55
$R_{fn}CH=CH_2$	⇒ $R_{fn}CH_2CH_2I + NaOH/C_2H_5OH$, 30 °C, 1 h → yield: 99%	56
$R_{fn}CH=CH_2$, $n = 4, 6, 8, 10$	⇒ $R_{fn}I + CH_2=CHSi(CH_3)_3$ → $R_{fn}CH_2CHISi(CH_3)_3$; + Bu_4NF →	57
$R_{f8}CH_2CH=CH_2$	⇒ $R_{f8}I + CH_2=CHCH_2Cl$ /AIBN → title olefin + adduct	58
$(CF_3)_3CCH_2CH=CH_2$	⇒ $(CF_3)_2C=CF_2/CsF + CH_2=CHCH_2I$ /diglyme → yield: 80%	59
$CF_3(CF_2)_2C(CF_3)_2CH_2CH=CH_2$	⇒ Alkylation of perfluoro-2-methyl-2-pentylcarbanion with alkyl and allyl halides. Study the effect of solvents and F^- -sources	60
$(C_2F_5)_2C(CF_3)OCH_2CH=CH_2$	⇒ $(C_2F_5)_2C(CF_3)OK + CH_2=CHCH_2Br/CH_3CN$, reflux → bp 120 °C	61
$(CF_3)_2NCH_2CH=CH_2$,	⇒ $(CF_3)_2N^-Cs^+ + CH_2=CHCH_2Br$ → yield: 44%, bp = 42 °C	62
$n-C_4F_9CH=CHC_4F_9-n$	• + Remains unaffected when heated at 130 °C with Et_2NH or Br_2 for several weeks, by <i>m</i> -chloroperbenzoic acid	63
$R_{fn}C\equiv CH$, $n = 4, 6$	⇒ $R_{fn}I + HC\equiv CC(CH_3)_2OH$ /electrocatal. → $R_{fn}CH=ClC(CH_3)_2OH$ → $R_{fn}C\equiv CC(CH_3)_2OH$ → overall yield: 55–60%	64
$C_8F_{17}C_6H_5$, etc.	⇒ $C_8F_{17}I + C_6H_6/K_2CO_3$, 2% Ru-C, 30 h, 170 °C → yield: 89%	65
$R_{f8}Ph$	⇒ $PhH + R_{f8}N=NR_{f8}/CF_2ClCFCl_2$, $h\nu$, 2 h → yield: 70%	66
$R_{fn}R$, ($R = Ar, Het$)	⇒ $2R_{fn}I + ArH/\sim 250$ °C, 15 h → $R_{fn}Ar + R_{fn}H + I_2$, yield: 60–65%	67
	⇒ $R_{fn}I + ArH + tBu_2O_2$, ~ 150 °C, 8 h → $R_{fn}Ar$, yield: 40–95%	67d
$R_{f8}C_6H_4CF_3$; $R_{f8}C_6H_3(CF_3)_2$ (<i>o</i> -, <i>m</i> - and <i>p</i> -; and 1,3,5-isomers)	⇒ $R_{fn}I + ArI/Cu$, DMSO/130–135 °C, 6 h → yield: 48–84%	68
$F_5S(CF_2)_6C_6H_5$	⇒ $F_5S(CF_2)_6I + C_6H_6$ (160–165 °C/14 d) → yield: 51% by GC	69
$R_{f8}CH_2CH_2Ph$	⇒ $PhMgCl + R_{f8}CH_2CH_2I/CuBr\cdot THF$, 18 h, r.t. → yield: 89%	70
$R_{f10}CH_2CH_2Ph$	⇒ $PhB(OH)_2 + R_{f10}CH_2CH_2I/Pd(PPh_3)_4$, $NaHCO_3$, $H_2O-CH_3OCH_2CH_2OCH_3$, 5 h → yield: 89%	71

Tab. 9.2-1 (continued)

Compound [C,F,H]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
$R_{fn}Ar$	$\Rightarrow ArBr + R_{fn}I/Cu, DMSO \rightarrow$ good yields	72
$R_{fn}CH_2CH_2Ar$ via $R_{fn}CH=CHAr$	$\Rightarrow ArX + CH_2=CHR_{fn}/Pd-cat \rightarrow ArCH=CHR_{fn};$ $+ H_2/Pd-C \rightarrow$	73
$(R_{fn}CH_2CH=CH)_xAr$, $n = 6, 8, 10$ $(R_{fn}CH_2CH_2CH_2)_xAr$; $x = 1-3$	$\Rightarrow [R_{fn}CH_2CH_2PPh_3]^+I^- + Ar(CHO)_x \rightarrow$ $(R_{fn}CH_2CH=CH)_xAr; + H_2/cat \rightarrow$ overall yield: 68–90%	74

Tab. 9.2-2. (Perfluoroalkyl)alkyl halides; perfluoroalkyl- and (perfluoroalkyl)alkyl aryl/benzyl halides

Compound [C,F,H,X]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
$R_{f3}CH_2I$	$\Rightarrow R_{f3}CH_2OTs + KI/\text{diethylene glycol}, T > 190^\circ C \rightarrow$ yield: 84%	75
$R_{fn}CH_2CH_2I$	$\Rightarrow R_{fn}I + CH_2=CH_2/290-390^\circ C$ for $n = 4, 6, 8, 10 \rightarrow$ yield: ~95%	76, 77
$R_{f6}CH_2CH_2CH_2I$	$\Rightarrow R_{f6}(CH_2)_3OH + KI, P_2O_5/H_3PO_4 \rightarrow$ yield: 88% (72% conversion)	56
$R_{f8}CH_2CH_2CH_2I$	$\Rightarrow R_{f8}(CH_2)_3OH + KI, P_2O_5/H_3PO_4; P_2O_5/SiO_2 \rightarrow$ yield: 70–85%	78
$R_{f8}CH_2CH_2CH_2CH_2I$	$\Rightarrow R_{f8}(CH_2)_3OH + KI, P_2O_5/H_3PO_4 (120^\circ C/4\text{ h}) \rightarrow$ yield: 92%	79
$F_5S(CF_2CF_2)_3CH_2CH_2I$	$\Rightarrow CH_2=CH_2 + F_5S(CF_2CF_2)_3I/^tBu_2O_2 \rightarrow$ yield: 28%	80
$1,3,5-BrC_6H_3(R_{f8})_2$	$\Rightarrow 1,3,5-Br_3C_6H_3 + 2 R_{f8}I + 4 Cu/DMF, 120^\circ C, 18\text{ h} \rightarrow$ yield: 60%	81
$1,3,5-BrC_6H_3(R_{f10})_2$	$\Rightarrow m-(R_{f10})_2C_6H_4 + NBS/H_2SO_4\cdot CF_3CO_2H, 50^\circ C, 8\text{ h} \rightarrow$ yield: 94%	82
$1,2,4,6-IC_6H_2[(CH_2)_3R_{f8}]_3;$ $1,2,4-, 1,2,5-; 1,3,4-$ $IC_6H_3[(CH_2)_3R_{f8}]_2$	$\Rightarrow C_6H_3(CH_2CH_2CH_2R_{f8})_3$ or $C_6H_4(CH_2CH_2CH_2R_{f8})_2 +$ I_2/H_5IO_6 in $AcOH, H_2SO_4/H_2O \rightarrow$ yields of respective iodoarenes: 61–97%	83
$3,5-(R_{f8})_2C_6H_3CH_2Br$	$\Rightarrow 3,5-(R_{f8})_2C_6H_3CH_2OH + PBr_3/THF \rightarrow$ yield: 62%	84

Tab. 9.2-3. Perfluoroalkylalkanols and ethers

Compound [C,F,H,O]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CH_2OH$	⇒ $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3 + NaBH_4/\text{ether} \rightarrow (81\%)$	85
$(CF_3)_3CCH_2OH$	⇒ $(CF_3)_3CH + CH_2O/Et_3N, 100\text{ }^\circ\text{C}, 55\text{ h} \rightarrow \text{no yield data given}$	86
$R_{fn}CH_2CH_2CH_2OH, n = 6, 8, 10$	⇒ One pot synthesis from $R_{fn}I$ and triallyl borate, yield: 74–79%	87
$(C_6F_{13}CH_2CH_2)_2C(CH_2OH)_2$	⇒ Preparation of and use for acetalization	88
$(R_{f8}CH_2CH_2)_2CHOH$	⇒ $C_8F_{17}CH_2CH_2I + Mg/\text{ultrasound}; + HCO_2Et \rightarrow \text{yield: } 93\%$	89
$R_{f8}CH_2CH_2C(CH_3)_2OH$ [$R_{f6}(CH_2)_n]_2C(CH_3)OH, n = 2, 3$	⇒ $R_f(CH_2)_nMgX + Me_2CO$ or $EtOAc \rightarrow$ used for the synthesis of F Boc-transfer reagents	90
$R_{f6}CH_2CH_2C(CH_3)_2OH,$ [$R_{fn}(CH_2)_2]_2C(CH_3)OH, n = 6, 8$	⇒ Conveniently prepared by the reaction of appropriate Grignard reagents with acetone and ethyl acetate, respectively	91
$R_{f6}CH_2CH_2C(CH_3)_2OH$	⇒ $R_{f6}I + CH_2=CHC(CH_3)_2OH/Cu, 120\text{ }^\circ\text{C} \rightarrow R_{f6}CH_2CH(I)C(CH_3)_2OH (83\%); + Bu_3SnH \rightarrow \text{yield: } 67\%$	92
$R_{fn}CH_2CH_2C(CH_3)_2OH, n = 4, 6, 8$	⇒ $R_{fn}CH=CH_2 + (CH_3)_2CHOH/\text{acetone}, h\nu, \text{r.t.}, 3\text{ d} \rightarrow \text{yield: } 91\%$	93
$(R_{f6}CH_2CH_2)_3COH$	⇒ $C_6F_{17}CH_2CH_2I + Mg/\text{ether}; + CH_3OC(O)OCH_3 \rightarrow \text{yield: } 40\%$	94
$3,5-(C_8F_{17})_2C_6H_3CH_2OH$	⇒ $1,3-(R_{f8})_2C_6H_3CO_2CH_3 + LiAlH_4/Et_2O, 5\text{ h reflux} \rightarrow \text{yield: } 90\%$	68
$C_8F_{17}-\begin{array}{c} Si(CH_3)_3 \\ \\ OH \\ \\ CH_3 \end{array}$	⇒ $CH_3COSi(CH_3)_3 + C_8F_{17}I/C_2H_5MgBr, -45\text{ }^\circ\text{C to r.t.} \rightarrow \text{yield: } 45\%, \text{mp} = 29\text{ }^\circ\text{C}$	95
$R_{f6}CH_2CH_2OCH(CH_3)CH_2CH(CH_3)_2$	⇒ •+ A new fluororous/organic amphiphilic ether solvent	96
$(CF_3)_3CCH_2OCH_2C(CF_3)_3$	⇒ $(CF_3)_2C=CF_2/CsF + (ClCH_2)_2O \rightarrow \text{yield: } 71\%, \text{bp} = 156\text{--}157\text{ }^\circ\text{C}$	97
$(CF_3)_3CCH_2OCH_3$	⇒ $(CF_3)_2C=CF_2 + ClCH_2OCH_3/CsF, \text{diglym}, 70\text{ }^\circ\text{C} \rightarrow \text{yield: } 90\%$ •+ $SO_3/H_2SO_4; \text{r.t.}, 1\text{ h} \rightarrow (CF_3)_3CCH_2OH, \text{yield: } 45\%$	98
$(CF_3)_3COCH_3, (CF_3)_3COC_2H_5$	⇒ $(CF_3)_3CONa + R_2SO_4/\text{tetraglyme} \rightarrow \text{yield: } \sim 95\%$	99
$R_{fn}CH_2CH(-O-)CH_2, n = 4, 6, 8$	⇒ (a) $R_{fn}I + CH_2=CHCH_2OAc \rightarrow R_{fn}CH_2CH(I)CH_2OAc + R_{fn}CH_2CH(OAc)CH_2I;$ (b) $+ KOH/\text{hexane} \rightarrow \text{yield: } 94\text{--}96\%$	100

Tab. 9.2-4. Fluorous mercaptanes, sulfides, sulfoxides, sulfonates, sulfonimides and selenides

Compound [C,F,H,S/Se(O)]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$R_{fn}CH_2SH$, $n = 2, 3$	⇒ $R_{fn}COX$ ($X = H, Cl$) + H_2S , 200 °C, 3000 atm → yield: 39–54%	101
$R_{f6}CH_2CH_2SH$	⇒ $R_{f6}(CH_2)_2I$ + H_2NCSNH_2 /dioxane → yield: 94%, unlike alcohol type solvents no foul-smelling byproducts are formed in dioxane!	102
$R_{f8}CH_2CH_2CH_2SH$	• + $(C_8H_{17})_4NAuCl_4/CF_3Ph + NaBH_4/H_2O$ → $(Au_x)[HS(CH_2)_3R_{f8}]_y$ First example for an isolable and fluorous soluble gold nanocluster	103
$F_5S(CF_2)_6CH_2CH_2SH$	⇒ $F_5S(CF_2)_6(CH_2)_2I + NaH/AcSH-THF$ → $F_5S(CF_2)_6(CH_2)_2SAC$; + $LiAlH_4/THF$ → overall yield: 90%	104
$R_{f7}SCH_3$	⇒ $R_{f7}C(O)SCH_3/CH_3CN, hv/(-CO)$ → yield: 81%	105
$R_{f8}CH_2CH_2SCH_3$	⇒ $R_{f8}CH_2CH_2SCOCH_3 + NaOCH_3$; CH_3I → yield: 94%	106
$R_{fn}SCH_2CH_2OH$; $n = 4, 6$	⇒ $HO(CH_2)_2SH + R_{fn}I/Na_2SO_3, HCO_2Na, DMF-H_2O$, r.t. →	107
$[R_{f8}(CH_2)_n]_2S$, $n = 2, 3$	⇒ $R_{f8}(CH_2)_nI + Li_2S/THF$ → yields: 67–71%	108
$ArSR_{fn}$, $n = 3$	⇒ $ArSH + R_{fn}I + NaOH, PhCH_2NEt_3Cl$ → yield: 83%	109
$ArSR_{fn}$, e.g.: $Ar = p-CH_3C_6H_4$, $n = 6$	⇒ (a) $ArSH + N(C_2H_5)_3 + R_{f6}Br/DMF, hv$ → yield: 52%; ⇒ (b) $ArSK + R_{f6}Br/DMF \sim 3$ atm → yield: 77%	110, 111
$R_{f8}(CH_2)_nSO(CH_2)_nR_{f8}$, $n = 2, 3$	⇒ $[R_{f8}(CH_2)_n]_2S + CH_3CO_3H$ → yield: 80–85%	108
$R_{fn}CH_2CH_2S(O)CH_3$, $n = 4, 6$	⇒ $(CH_3)_2S_2/NaBH_4 + R_{fn}(CH_2)_2I \rightarrow R_{fn}(CH_2)_2SCH_3$; + H_2O_2/CH_3OH → overall yield: 71%	112
$R_{f7}CH_2OSO_2CF_3$	⇒ $R_{f7}CH_2OH + (CF_3SO_2)_2O/py, CH_2Cl_2$ → yield: 92%	113
$R_{f7}CH_2OSO_2C_4F_9$	⇒ $R_{f7}CH_2OH + R_{f4}SO_2F/TEA, ether$ → yield: 95%	114
$R_{f8}CH_2CH_2CH_2OTs$	⇒ $R_{f8}CH_2CH_2CH_2OH + TsCl/CH_2Cl_2-aq.NaOH$ → yield: 70%	115
$(R_{fn}SO_2)_2NH$, $n = 2, 4, 8$	⇒ Products were obtained after high-vacuum sublimation or short-path distillation from conc. H_2SO_4	116
$2,4-(R_{f8})_2C_6H_3SeC_4H_9$	⇒ $2,4-I_2C_6H_3NH_2 + R_{f8}I/Cu, DMSO, 120$ °C → $2,4-(R_{f8})_2C_6H_3NH_2$; + $NaNO_2, HBr, CuBr$ → $2,4-(R_{f8})_2C_6H_3Br$; + $C_4H_9SeLi/THF, -80$ to -25 °C → $2,4-(R_{f8})_2C_6H_3SeC_4H_9$, overall yield: 36%	117
$3,5-(R_{f8})_2C_6H_3SeC_4H_9$	⇒ Prepared by multiple step synthesis from $3,5-I_2C_6H_3NH_2$ and used as a catalyst in Bayer-Villiger oxidation	118

Tab. 9.2-5. Fluorous amines, anilines, pyridines; phosphines and phosphites

Compound [C,F,H,N/P(O)]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$R_{f7}CH_2NH_2$, $(R_{f7}CH_2)_2NH$	⇒ Precursors of tetrasubstituted ureas, thermally stable fluids, recoverable in 99% after a 63 h at 270 °C test	119
$(R_{f9}CH_2)_2NH$	⇒ $(R_{f9}CO)_2NH + LiAlH_4 \rightarrow$ no yield data reported, mp = 85–86 °C	120
$[(CF_3)_3C]_2NH$	⇒ multistep synthesis/bp = 100–101 °C/	121
$R_{f7}CH_2N(CH_3)_2$	⇒ $R_{f7}CSN(CH_3)_2 + BH_3/diglyme \rightarrow$ yield: 59%, GC purity: 99%	122
$(CF_2)_4NCH_2CF_2CF_3$	⇒ $CF_2CF_2CF_2CF=N + KF + CF_3CF_2CH_2OSO_2CF_3 \rightarrow$ yield: 71%	123
$CF_3CF_2(CF_3)NCH_3$	⇒ $CF_3CF=NCF_3 + CsF + (CH_3)_2SO_4/CH_3CN \rightarrow$ yield: 46%	124
$[(CF_3)_3CCH_2]_3N$	⇒ $(CF_3)_2C=CF_2 + CsF + (ClCH_2)_3N/diglyme \rightarrow$ yield: 32%	97
$R_{fn}CH_2CH_2NH_2$, $n = 2, 4, 6, 8$	⇒ $R_{fn}CH_2CH_2I + NaN_3 \rightarrow R_{fn}CH_2CH_2N_3$; $H_2/Pt \rightarrow$	125
$NH_{3-x}[(CH_2)_mR_{f8}]_x$, $m = 3-5$, $x = 1, 2$ $N[(CH_2)_mR_{f8}]_3 = N(R_{fh})_3$	⇒ $R_{fh}(CH_2)_{m-1}CHO + NH(R_{fh})_2$ or $H_2NCH_2Ph/Na(AcO)_3BH \rightarrow N(R_{fh})_3$ or $NH_{2-x}(CH_2Ph)[(CH_2)_mR_{f8}]_x$; + $H_2/Pd-C \rightarrow$ 78–91%	126
$[(R_{f6}CH_2CH_2)_3SiCH_2CH_2CH_2]_2NH$	⇒ $[(R_{f6}(CH_2)_2Si(CH_2)_3)_2NCOCF_3 + LiAlH_4/ether \rightarrow$ yield: 97% •+ RNCO \rightarrow fluorous soluble ureas, easy to remove by extraction	127
$(R_{f8}CH_2CH_2CH_2)_2NCH_3$	⇒ $R_{f8}(CH_2)_3NCH_3 + R_{f8}(CH_2)_3I/THF$, 60 °C, 24 h \rightarrow yield: 84%	128
$[(R_{f8}CH_2CH_2CH_2)_3NCH_3]^+CH_3OSO_3^- = R_F^+CH_3OSO_3^-$	⇒ •+ $Na_{12}\{[WZnM_2(H_2O)_2](ZnW_9O_{34})_2\} \rightarrow$ fluorous soluble salts of polyoxometalates: e.g. $(R_F^+)_{12}[WZn_3(H_2O)_2](ZnW_9O_{34})_2]^{12-}$	129
2,4,6- $(R_{f8})_3C_6H_2NH_2$, 4,2,6- $(CF_3)(R_{f8})_2C_6H_2NH_2$, 4,2,6- $(Me_3C)(R_{f8})_2C_6H_2NH_2$	⇒ $C_6H_5N(CH_3)_2$, 4- $CF_3C_6H_4NH_2$ or $Me_3CC_6H_4NH_2 + R_{f8}I/Cu_2O$, DMSO, 130 °C, 1 to 3 d \rightarrow yield: 45, 65, and 27%	130
2,6- and 3,5- $(C_8F_{17}CH_2CH_2)_2C_5H_3N$ $s-[R_{f8}(CH_2)_2]_3py$, 2,6- $[R_{f8}(CH_2)_3]_2py$	⇒ $C_8F_{17}CH_2CH_2ZnI/THF + Br_2py/Cl_2Pd(PPh_3)_3 \rightarrow$ yield: 31–85% ⇒ $py(CHO)_x \rightarrow (R_{f8}CH_2CH=CH)_xpy$; + $H_2/Pd-C \rightarrow$ yield: 93%	131
2,6- $(R_{f6})_2py$	⇒ 2,6- $Br_2py + C_6F_{13}I/Cu$, DMSO, 125 °C \rightarrow yield: 89%	132
$P[(CH_2)_\gamma R_{fn}]_3$, $\gamma = 2$, $n = 6, 8, 10$; $\gamma = 3, 4$, $n = 8$	⇒ $PH_3 + CH_2=CH(CH_2)_xR_{fn}/AIBN$ or $VAZO \rightarrow$ yield: 63–81%	133, 134
$R_{f8}(CH_2)_mPH_2$; $R_{f8}(CH_2)_mP[(CH_2)_{m'}R_{f8}]_2$	⇒ $LiPH_2 + R_{f8}(CH_2)_mI \rightarrow R_{f8}(CH_2)_mPH_2$; + $R_{f8}(CH_2)_{m'-2}CH=CH_2/AIBN$ or $VAZO \rightarrow$ good yields: $m = 2-4$, $m/m' = 3/2, 2/3, 4/3, 3/4$	79
$(R_{f8}CH_2CH_2O)_3P$	⇒ $R_{f8}CH_2CH_2OH + PCl_3/py-ether \rightarrow$ yield: 55%	133

Tab. 9.2-6. Fluorous boron-, silicon-, tin-, lithium-, zinc-, and magnesium compounds

Compound [C,F,H,B/Si/Sn/Metal]	Remarks ("⇒" for synthesis of; "• + " for reaction of; etc.)	Ref.
$(R_{f10})_2C_6H_3B(OH)_2$	⇒ Multistep synthesis: $1,3-C_6H_4I_2 \rightarrow 1,3-C_6H_4(R_{f10})_2 \rightarrow 1,3,5-BrC_6H_3(R_{f10})_2 \rightarrow 1,3,5-(RO)_2BC_6H_3(R_{f10})_2 \rightarrow$	82
$NaB[C_6H_4(SiMe_2CH_2CH_2C_6F_{13})-p]_4$, $NaB[C_6H_4C_6F_{13}-p]_4$	⇒ $ArBr + {}^tBuLi/ether, -78\text{ }^\circ C \rightarrow ArLi/ether;$ $+ BF_3 \cdot O(C_2H_5)_2; \rightarrow LiB[Ar]_4/ether; + NaCl-H_2O \rightarrow$	135 136
$NaB[C_6H_3(C_6F_{13})_2-3,5]_4$	⇒ Multistep procedure starting from $1,3-C_6H_4I_2$ and $C_6F_{13}I$	137
$(R_{f6}CH_2CH_2)_3SiH$	• + $(CH_2=CHCH_2)_2NCOCF_3/H_2PtCl_6, 80\text{ }^\circ C, 12\text{ h} \rightarrow [(R_{f6}CH_2CH_2)_3SiCH_2CH_2CH_2]_2NCOCF_3$, yield: 33–37%	127
$R_{fn}Si(CH_3)_3, n = 1-3$	⇒ $(CH_3)_3SiCl + R_{fn}Br/PhCN; + [(C_2H_5)_2N]_3P/PhCN \rightarrow$	138
$(R_{f6}CH_2CH_2)_3SiCH_2CH=CH_2$	• + Useful perfluoroalkyl-anion transfer reagents	139
$(R_{f6}CH_2CH_2)_3SiCH_2CH=CH_2$	⇒ $(R_{f6}CH_2CH_2)_3SiBr + CH_2CH=CH_2MgBr \rightarrow$ yield: 98%	140
$p-(R_{f6}CH_2CH_2)_3SiC_6H_4CH_2Br$	⇒ $[R_{f6}(CH_2)_2]_3SiBr + p-TolMgBr \rightarrow [R_{f6}(CH_2)_2]_3SiTol-p; + Br_2 \rightarrow$	141
$(R_{f10}CH_2CH_2)_3SiC_6H_4CO_2H$	⇒ Multistep synthesis from $R_{f10}CH_2CH_2I$ and $HSiCl_3$	142
$R_{fn}(CH_2)_2(i-Pr)_2SiBr, n = 6, 8$	⇒ $R_{fn}(CH_2)_2Si({}^iPr)_2H + Br_2/FC-72 \rightarrow$ • Used up immediately	143
$(R_{fn}CH_2CH_2)_{3-x}Si(CH_3)_xBr, n = 6, 8; x = 0, 1, 2$	⇒ $R_{fn}(CH_2)_2I + Mg/ether \rightarrow R_{fn}(CH_2)_2MgI;$ $+ HSi(CH_3)_{2-x}Cl_{x+1} \rightarrow (R_{fn}CH_2CH_2)_{3-x}Si(CH_3)_xH;$ $+ Br_2/hexane \rightarrow$ product	144
$R_{f10}CH_2CH_2Si(CH_3)_2Cl$	⇒ $R_{f10}CH=CH_2 + HSi(CH_3)_2Cl/RhCl(PPh_3)_3 \rightarrow$ yield: 85%	145
$R_{f3}C(CF_3)_2CH_2CH_2CH_2SiMe_2Cl$	⇒ $R_{f3}C(CF_3)_2CH_2CH=CH_2 + HSiMe_2Cl/H_2PtCl_6/$ heating \rightarrow 81%	146
$[R_{f8}CH_2CH_2(CH_3)_2Si]_2O$	⇒ $R_{f8}I + [CH_2=CH(CH_3)_2Si]_2O/AIBN \rightarrow [R_{f8}CH_2CHI(CH_3)_2Si]_2O; + Bu_3SnH, 80\text{ }^\circ C, 2\text{ h} \rightarrow$	147
$SiO_2(-O)_3Si(CH_2)_3NHC(O)-CF(CF_3)OCF(CF_3)OCF(CF_3)OCF_3F_7$	⇒ $Silica(-O)_3Si(CH_2)_3NH_2 + R_fOR_fC(O)F \rightarrow$	148
$[R_{f6}(CH_2)_3]_3SnCH_2CH=CH_2$	• + Useful fluorous allyl-transfer reagent	149
$4-RC_6H_4Sn[(CH_2)_2R_{f6}]_3$	⇒ • + $ArOSO_2CF_3/DMF-THF, PdCl_2(PPh_3)_2, LiCl \rightarrow 4-RC_6H_4Ar$	150
$(R_{f6}CH_2CH_2)_3SnR, R = Ph, Br, H$	⇒ $Cl_3SnPh + R_{f6}CH_2CH_2MgI \rightarrow (R_{f6}CH_2CH_2)_3SnPh;$ $+ Br_2 \rightarrow (R_{f6}CH_2CH_2)_3SnBr; + LiAlH_4 \rightarrow$ overall yield: 65%	151
$(R_{f6}CH_2CH_2)_3SnN_3$	⇒ $(R_{f6}CH_2CH_2)_3SnBr + NaN_3, ether-H_2O, 25\text{ }^\circ C \rightarrow$ yield: 97%	152
$Sn[N(SO_2C_8F_{17})_2]_4$	• + Catalyst for Bayer-Villiger oxidation	153
$R_{fn}CH_2CH_2Li/Et_2O, n = 6, 8$	⇒ $R_{fn}(CH_2)_2I/{}^tBuLi, ether; + HSi({}^iPr)_2Cl \rightarrow R_{fn}(CH_2)_2Si({}^iPr)_2Hs$	143
$R_{f8}CH_2CH_2ZnI/THF$	⇒ $R_{fn}CH_2CH_2I + Zn/THF, BrCH_2CH_2Br, (CH_3)_3CCl \rightarrow$	131
$R_{f6}CH_2CH_2MgI$	• Precursor for the synthesis of the first fluorous tin hydride/azide: $\{(R_{f6}CH_2CH_2)SnX, X = H, N_3\}$ applied in "Fluorous Synthesis"	151, 154

Tab. 9.2-7. Fluorous aldehydes and ketones

Compound [C,F,H,O]	Remarks ("⇒" for synthesis of; "●+" for reaction of; etc.)	Ref.
C ₈ F ₁₇ CHO	⇒ C ₈ F ₁₇ I + (CH ₃) ₂ NCHO/Al-PbBr ₂ , r.t. → yield: 95%	155
R _{fn} CHO, n = 1, 2, 3, 7	⇒ R _{fn} CO ₂ R + LiAlH ₄ /ether, -78 °C, "inverse addition" → 70–76%	156
R _{fn} CH ₂ CHO	⇒ R _{fn} I + CH ₂ =CHOAc/AIBN, 4 h, 80 °C → R _{fn} CH ₂ CHIOAc; + CH ₂ =CHCO ₂ H/C ₂ H ₂ Cl ₄ , reflux, 12 h → aldehyde yield: 85%	157
R _{f6} CH(CH ₃)CHO	⇒ R _{f6} CH=CH ₂ + CO/H ₂ -cat → 78% ee at 21% conversion; cat: a polymer supported (R,S)-BINAPHOS-Rh(I) complex	158
C _n F _{2n+1} (CH ₂) _m CHO, m = 1–4	⇒ Oxidation of C _n F _{2n+1} (CH ₂) _m CH ₂ OH by (a), (b) or (c) methods: (a) Swern, (b) PyH ⁺ CrO ₃ Cl ⁻ , (c) Dess-Martin periodinane	159, 126
3,5-(C ₈ F ₁₇) ₂ C ₆ H ₃ CHO	⇒ 3,5-(R _{f8}) ₂ C ₆ H ₃ CH ₂ OH + PyH ⁺ CrO ₃ Cl ⁻ /CH ₂ Cl ₂ → yield: 85%	68
R _{fn} COCH ₃ , R _{fn} COCH ₂ COR _{fm}	⇒ R _{fn} CO ₂ H + CH ₃ MgBr → R _{fn} COCH ₃ ; + R _{fm} CO ₂ C ₂ H ₅ , NaOC ₂ H ₅ → good overall yields: (a) n = m = 6, (b) n, m = 6, 1; n = m = 6, 7	160
R _{f8} CH ₂ CH ₂ COCF ₃	⇒ R _{f8} CH ₂ CH ₂ I + Mg/ether, CF ₃ CO ₂ CH ₃ → yield: 32%	161
F[CF(CF ₃)CF ₂ O] _n CF(CF ₃)COCH ₂ -COCH ₃ , n = 1–4	⇒ F[CF(CF ₃)CF ₂ O] _n CF(CF ₃)CO ₂ CH ₃ + CH ₃ COCH ₃ /NaH → no yield data reported	162

Tab. 9.2-8. Fluorous carboxylic acids

Compound [C,F,H,O]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$R_{fn}CO_2H$	$\Rightarrow R_{fn}CF_2I + XSO_3H$ ($X = Cl, F$) $\rightarrow R_{fn}CF_2OSO_2X$; $+ H_2O \rightarrow$	163
$R_{fn}CO_2H$, $n = 2, 3, 5, 6, 7, 11$	$\Rightarrow R_{fn+1}I(Br) + \text{Rongalite-NaHCO}_3/\text{DMF-H}_2\text{O} \rightarrow$ yield: 51–86%	164
$C_nF_{2n+1}CO_2H$, $n = 4, 6, 8$	$\Rightarrow C_nF_{2n+1}I + Zn-Cu/CO_2, (CH_3O)_3PO, -20^\circ C \rightarrow$ yield: 91%	165
$(CF_3)_2CFOCF(CF_3)CO_2H$ (+)- and (–)-PIPA	\Rightarrow (+)-PIPA and (–)-PIPA have been prepared from CF_3COCF_3 and $CF_3CF_2CF_2O$ precursors by a multistep synthesis	166
$C_6F_{13}CH_2CO_2H$	$\Rightarrow R_{f6}(CH_2)_2OH + CrO_3/H_2SO_4, \text{acetone-ether} \rightarrow$ yield: 98% • + $Rh_2(OAc)_4/\text{toluene}, 110^\circ C (-4 \text{ AcOH}) \rightarrow$ $(R_{f6}CH_2CO_2)_4Rh_2$	167, 168
$(CF_3)_3COCH_2CO_2H$	$\Rightarrow (CF_3)_2CCF_2O + HF \rightarrow (CF_3)_3COH$; + $ClCH_2CO_2R \rightarrow$	169
$R_{fn}(CH_2)_mOCH_2CO_2H$, $n/m = 7/1, 8/2, 10/2$	$\Rightarrow R_{fn}(CH_2)_mOH + BrCH_2CO_2H/NaH, THF, \text{r.t.} \rightarrow$ yield: 70–96% • + $BH_3/THF, 0^\circ C \text{ to r.t.} \rightarrow R_{fn}(CH_2)_mO(CH_2)_2OH$, yield: 79–96%	170
$R_{fn}CH_2CH_2CO_2H$, $n = 6, 8, 10$	$\Rightarrow R_{fn}CH_2CH_2I + Mg/\text{ether} \rightarrow R_{fn}CH_2CH_2MgI$; + $CO_2 \rightarrow$ $\Rightarrow R_{f6}(CH_2)_3OH + NaIO_4, \text{cat-RuCl}_3 \rightarrow$ yield: 64% • + $SOCl_2 \rightarrow R_{f6}(CH_2)_2COCl$; + ferrocene/ $AlCl_3 \rightarrow$ $-(R_f\text{-acyl})_{1,2}Fc$	171
$(C_8F_{17}CH_2CH_2CH_2)_2CH_2CO_2H$	$\Rightarrow R_{f8}(CH_2)_3I + CH_2(CO_2C_2H_5)_2 \rightarrow \rightarrow \rightarrow$ overall yield: 58%	172
$C_8F_{17}CH_2CH_2CON(CH_2CH_2CH_2-$ $C_8F_{17})CH_2CH_2CO_2H$	\Rightarrow Used as a protective group for oligosaccharide synthesis • Precursor for new fluorous supports for peptide synthesis	173
$3,4,5-[C_8F_{17}(CH_2)_4O]_3C_6H_2CO_2H$	\Rightarrow Preparation and use for Mitsunobu-inversion of chiral <i>sec</i> -alcohols	174

Tab. 9.2-9. Fluororous esters and carbonic acid derivatives

Compound [C,F,H,O]	Remarks ("⇒" for synthesis of; "•+" for reaction of; etc.)	Ref.
$R_{fn}CO_2C_2H_5$, $n = 4, 6, 8$	$\Rightarrow R_{fn}I + ClCO_2C_2H_5 + (C_2H_5O)_2CO + Zn-Cu \rightarrow$ yield: 50–70%	175
$Br(CF_2)_6CO_2C_2H_5$	$\Rightarrow Br(CF_2)_6CCl_3 + SO_3/H_2SO_4; + C_2H_5OH \rightarrow$ yield: 67%	176
$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$	$\Rightarrow C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF + CH_3OH/Na_2CO_3,$ MgSO ₄ , silica gel \rightarrow yield: 86%	85
$R_{f8}CH_2CH_2CH(CO_2CH_3)_2$	$\Rightarrow R_{f8}CH_2CH_2I + CH_2(CO_2CH_3)_2/NaH$ or K_2CO_3 in THF \rightarrow high yields (~85%) with negligible elimination and dialkylation	177
$R_{f8}(CH_2)_nCO_2CH_2CF_3$, $n = 1, 2$	$\Rightarrow R_{f8}CH_2CH_2OH \rightarrow \sim CH_2OTs \rightarrow \sim CH_2Br \rightarrow$ $\sim CH_2MgBr \rightarrow \sim CH_2CO_2H \rightarrow \sim CH_2COCl \rightarrow$ title ester, overall yield: 55%	178
$(CF_3)_3CCO_2C_2H_5$	$\Rightarrow (CF_3)_2C=CF_2/CsF + ClC(O)OC_2H_5 \rightarrow$ yield: 76%, bp = 106 °C	179
$4-R_{f8}CH_2CH_2C_6H_4CO_2CH_3$	$\Rightarrow 4-BrC_6H_4CO_2CH_3 + R_{f8}CH=CH_2/Pd-cat, NaOAc,$ DMF, 125 °C, 14 h, $\rightarrow R_{f8}CH=CH_2C_6H_4CO_2CH_3$ (72%); $+ H_2/Pd-C \rightarrow$ (88%)	180
$(CF_3)_3CCH_2CH_2CO_2CH_3$	$\Rightarrow (CF_3)_3CH + CH_2=CHCO_2CH_3/(C_2H_5)_3N \rightarrow$ yield: 30%	181
$3,5-(C_8F_{17})_2C_6H_3CO_2CH_3$	$\Rightarrow R_{f8}I + 3,5-Br_2C_6H_3CO_2CH_3 + Cu/DMSO,$ 135 °C \rightarrow yield: 79%	68
$R_{f6}CH_2CH_2OCOCl$	$\Rightarrow R_{f6}CH_2CH_2OH + COCl_2/toluene, reflux 24 h \rightarrow$ yield: ~95%	182
$(CF_3)_3COCOCl$	$\Rightarrow (CF_3)_3COK + COCl_2/mesitylene \rightarrow$ yield: 54%	183
$R_{f7}CH_2NCO$	$\Rightarrow R_{f7}CH_2NH_2 + COCl_2 \rightarrow$ yield: 78%, bp = 166–168 °C	42
$R_{f9}CH_2NCO$	$\Rightarrow R_{f9}CH_2NH_2 + COCl_2/dioxane \rightarrow$ mp = 46–47 °C	184
$(C_7F_{15}CH_2)_2NCOCl$	$\Rightarrow (C_7F_{15}CH_2)_2NH + excess COCl_2/autogenous$ pressure, 140 °C, 14 h \rightarrow yield: 100%, mp = 22 °C, bp = 70 °C/0.1 mmHg	119
$R_{fn}CH_2CH_2N=C=NCH_2CH_2R_{fn},$ $n = 4, 6, 8$	$\Rightarrow R_{fn}(CH_2)_2N_3 + PPh_3/THF, < r.t. \rightarrow$ $R_{fn}(CH_2)_2N=PPh_3; + CS_2 \rightarrow$ $\Rightarrow [R_{fn}(CH_2)_2NH]_2CO + Ph_3PBr_2 + N(C_2H_5)_3$ in $CH_2Cl_2/C_6F_{14} \rightarrow$	185, 186
$R_{fn}(CH_2)_mO_2CNHNHCO_2(CH_2)_mR_{fn}$ $n/m = 3/1, 4/2, 6/2, 6/3$	• + NBS or $Br_2/py, CH_2Cl_2 \rightarrow$ $R_{fn}(CH_2)_mO_2CN=NCO_2(CH_2)_mR_{fn};$ yield: 79–100%; used for fluororous Mitsunobu reaction	182, 187

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